

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
26 June 2003 (26.06.2003)

PCT

(10) International Publication Number  
WO 03/051984 A1

(51) International Patent Classification<sup>7</sup>: C08L 23/10, C08F 297/08

(74) Agent: GAVERINI, Gaetano; Basell Poliolefine Italia S.p.A., Intellectual Property, Via Pergolesi, 25, I-20124 Milano (IT).

(21) International Application Number: PCT/EP02/14068

(81) Designated States (national): AU, BR, CA, CN, CO, CZ, HU, ID, IL, IN, JP, KR, MX, NO, PH, PL, RO, RU, SG, SK, UA, US, YU, ZA.

(22) International Filing Date:  
11 December 2002 (11.12.2002)

(84) Designated States (regional): European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR).

(25) Filing Language: English

Declarations under Rule 4.17:

(26) Publication Language: English

— as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations  
— of inventorship (Rule 4.17(iv)) for US only

(30) Priority Data:  
01130179.3 19 December 2001 (19.12.2001) EP

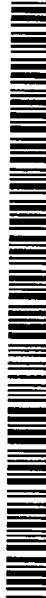
Published:

(71) Applicant (for all designated States except US): BASELL POLIOLEFINE ITALIA S.P.A. [IT/IT]; Via Pergolesi, 25, I-20124 Milano (IT).

— with international search report

(72) Inventors; and  
(75) Inventors/Applicants (for US only): PELLICONI, Antonio [IT/IT]; Via Volta, 22, I-45030 S.M. Maddalena (IT). CAGNANI, Camillo [IT/IT]; Via Matteotti, 5, I-47013 Dovadola (IT).

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.



WO 03/051984 A1

(54) Title: IMPACT-RESISTANT POLYOLEFIN COMPOSITIONS

(57) Abstract: Polyolefin compositions comprising (percent by weight): 1) 55 % - 90 % of a crystalline propylene homopolymer or copolymer containing up to 15 % of ethylene and/or C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s); 2) 10 % - 45 % of a blend of a copolymer of propylene with more than 15 % up to 40 % of ethylene (copolymer (a)), and a copolymer of ethylene with one or more C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s) containing from 10 % to 40 % of said C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s) (copolymer (b)), wherein the weight ratio (a)/(b) is from 1/4 to 4/1.

## IMPACT-RESISTANT POLYOLEFIN COMPOSITIONS

The present invention concerns polyolefin compositions comprising a crystalline propylene polymer component selected from propylene homopolymers and propylene-ethylene and/or other  $\alpha$ -olefin random copolymers, a copolymer of propylene with up to 40% by weight of ethylene and a copolymer of ethylene with  $C_4$ - $C_{10}$   $\alpha$ -olefins.

The compositions of the present invention present a unique balance of processability, mechanical properties and optical properties. In addition they present low/very low blush, reduced blooming and low content of fraction extractable in organic solvents.

The said compositions can be easily processed by injection-molding and can be used for several applications, including housewares and toys, and in particular for food-contact applications.

Compositions comprising polypropylene and a rubbery phase formed by an elastomeric copolymer of ethylene with  $\alpha$ -olefins are already known in the art, and described in particular in European patents 170 255 and 373 660, and in WO 01/19915. Said compositions present impact resistance and, in the case of European patent 373 660 and WO 01/19915, transparency values interesting for many applications, however the overall balance of properties is still not totally satisfactory in the whole range of possible applications, in view of the high standards required by the market. Therefore there is a continuous demand for compositions of this kind with improved properties.

A new and valuable balance of properties has now been achieved by the polyolefin compositions of the present invention, comprising (percent by weight):

- 1) 55%-90%, preferably 62%-85%, of a crystalline propylene homopolymer or copolymer containing up to 15%, preferably up to 10%, of ethylene and/or  $C_4$ - $C_{10}$   $\alpha$ -olefin(s);
- 2) 10%-45%, preferably 15%-40%, of a blend of a copolymer of propylene with more than 15% up to 40% of ethylene, preferably from 18% to 35% of ethylene (copolymer (a)), and a copolymer of ethylene with one or more  $C_4$ - $C_{10}$   $\alpha$ -olefin(s) containing from 10% to 40%, preferably from 10% to 35%, of said  $C_4$ - $C_{10}$   $\alpha$ -olefin(s) (copolymer (b)), wherein the weight ratio (a)/(b) is from 1/4 to 4/1, preferably from 1/2.5 to 2.5/1, more preferably from 1/2 to 2/1.

From the above definitions it is evident that the term "copolymer" includes polymers containing more than one kind of comonomers.

As previously said, the compositions of the present invention can be easily converted into various kinds of finished or semi-finished articles, in particular by using injection-molding techniques, as they possess relatively high values of MFR, associated with the said high balance of properties (in particular, of flexural modulus, impact resistance, ductile/brittle transition temperature and haze). The compositions of the present invention having values of MFR (230 °C, 2.16 Kg) of the overall composition equal to or higher than 4 g/10 min., in particular equal to or higher than 5 g/10 min., are preferred.

Other preferred features for the compositions of the present invention are:

- content of polymer insoluble in xylene at room temperature (23 °C) (substantially equivalent to the Isotacticity Index) for component 1): not less than 90%, in particular not less than 93% for propylene copolymers and not less than 96% for propylene homopolymers, said percentages being by weight and referred to the weight of component 1);
- Intrinsic Viscosity  $[\eta]$  of the fraction (of the overall composition) soluble in xylene at room temperature: 0.8 to 2.5 dl/g, more preferably, when high transparency is desired, 0.8 to 1.6, most preferably 0.8 to 1.5 dl/g.

The compositions of the present invention preferably present at least one melt peak, determined by way of DSC (Differential Scanning Calorimetry), at a temperature higher than 145-150°C.

Moreover, the compositions of the present invention preferably have:

- a total content of ethylene from 10% to 30% by weight;
- a total content of C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s) of 8% by weight or less, more preferably of 5% by weight or less;
- a Flexural Modulus from 600 to 1300 MPa;
- Izod values at 23°C of at least 4 KJ/m<sup>2</sup>;
- tensile stress at yield: 15-30 MPa;
- elongation at break: higher than 40%, more preferably higher than 100%;
- substantially no whitening (blush) when bending a plaque 1mm thick;
- fraction soluble in xylene at room temperature: less than 25%, more preferably less than 23% by weight.

The ductile/brittle transition temperature is generally equal to or lower than -25 °C, the lower limit being indicatively of about -60 °C.

The said  $C_4$ - $C_{10}$   $\alpha$ -olefins, that are or may be present as comonomers in the components and fractions of the compositions of the present invention, are represented by the formula  $CH_2=CHR$ , wherein R is an alkyl radical, linear or branched, with 2-8 carbon atoms or an aryl (in particular phenyl) radical.

Examples of said  $C_4$ - $C_{10}$   $\alpha$ -olefins are 1-butene, 1-pentene, 1-hexene, 4-methyl-1-pentene and 1-octene. Particularly preferred is 1-butene.

The compositions of the present invention can be prepared by a sequential polymerization, comprising at least three sequential steps, wherein components 1) and 2) are prepared in separate subsequent steps, operating in each step, except the first step, in the presence of the polymer formed and the catalyst used in the preceding step. The catalyst is added only in the first step, however its activity is such that it is still active for all the subsequent steps.

In particular, component 2) requires two sequential step, one for preparing copolymer (a) and the other for preparing copolymer (b).

Preferably component 1) is prepared before component 2).

The order in which copolymers (a) and (b), constituting component 2), are prepared is not critical.

The polymerization, which can be continuous or batch, is carried out following known techniques and operating in liquid phase, in the presence or not of inert diluent, or in gas phase, or by mixed liquid-gas techniques. Preferably component 1) is prepared in liquid phase, and component 2) is prepared in gas phase.

Reaction time, pressure and temperature relative to the two steps are not critical, however it is best if the temperature is from 20 to 100 °C. The pressure can be atmospheric or higher.

The regulation of the molecular weight is carried out by using known regulators, hydrogen in particular.

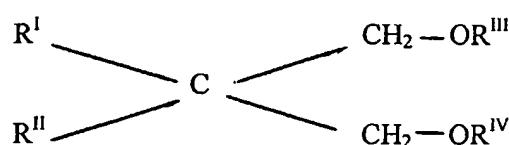
Such polymerization is preferably carried out in the presence of stereospecific Ziegler-Natta catalysts. An essential component of said catalysts is a solid catalyst component comprising a titanium compound having at least one titanium-halogen bond, and an electron-donor compound, both supported on a magnesium halide in active form. Another essential component (co-catalyst) is an organoaluminum compound, such as an aluminum alkyl compound.

An external donor is optionally added.

The catalysts generally used in the process of the invention are capable of producing polypropylene with an isotactic index greater than 90%, preferably greater than 95%. Catalysts having the above mentioned characteristics are well known in the patent literature; particularly advantageous are the catalysts described in US patent 4,399,054 and European patent 45977.

The solid catalyst components used in said catalysts comprise, as electron-donors (internal donors), compounds selected from the group consisting of ethers, ketones, lactones, compounds containing N, P and/or S atoms, and esters of mono- and dicarboxylic acids. Particularly suitable electron-donor compounds are phthalic acid esters, such as diisobutyl, dioctyl, diphenyl and benzylbutyl phthalate.

Other electron-donors particularly suitable are 1,3-diethers of formula:



wherein R<sup>I</sup> and R<sup>II</sup> are the same or different and are C<sub>1</sub>-C<sub>18</sub> alkyl, C<sub>3</sub>-C<sub>18</sub> cycloalkyl or C<sub>7</sub>-C<sub>18</sub> aryl radicals; R<sup>III</sup> and R<sup>IV</sup> are the same or different and are C<sub>1</sub>-C<sub>4</sub> alkyl radicals; or are the 1,3-diethers in which the carbon atom in position 2 belongs to a cyclic or polycyclic structure made up of 5, 6 or 7 carbon atoms and containing two or three unsaturations.

Ethers of this type are described in published European patent applications 361493 and 728769.

Representative examples of said dieters are 2-methyl-2-isopropyl-1,3-dimethoxypropane, 2,2-diisobutyl-1,3-dimethoxypropane, 2-isopropyl-2-cyclopentyl-1,3-dimethoxypropane, 2-isopropyl-2-isoamyl-1,3-dimethoxypropane, 9,9-bis (methoxymethyl) fluorene.

The preparation of the above mentioned catalyst components is carried out according to various methods.

For example, a  $MgCl_2 \cdot nROH$  adduct (in particular in the form of spheroidal particles) wherein n is generally from 1 to 3 and ROH is ethanol, butanol or isobutanol, is reacted with an excess of  $TiCl_4$  containing the electron-donor compound. The reaction temperature is generally from 80 to 120 °C. The solid is then isolated and reacted once more with  $TiCl_4$ , in

the presence or absence of the electron-donor compound, after which it is separated and washed with aliquots of a hydrocarbon until all chlorine ions have disappeared.

In the solid catalyst component the titanium compound, expressed as Ti, is generally present in an amount from 0.5 to 10% by weight. The quantity of electron-donor compound which remains fixed on the solid catalyst component generally is 5 to 20% by moles with respect to the magnesium dihalide.

The titanium compounds which can be used for the preparation of the solid catalyst component are the halides and the halogen alcoholates of titanium. Titanium tetrachloride is the preferred compound.

The reactions described above result in the formation of a magnesium halide in active form. Other reactions are known in the literature, which cause the formation of magnesium halide in active form starting from magnesium compounds other than halides, such as magnesium carboxylates.

The Al-alkyl compounds used as co-catalysts comprise the Al-trialkyls, such as Al-triethyl, Al-trisobutyl, Al-tri-n-butyl, and linear or cyclic Al-alkyl compounds containing two or more Al atoms bonded to each other by way of O or N atoms, or SO<sub>4</sub> or SO<sub>3</sub> groups.

The Al-alkyl compound is generally used in such a quantity that the Al/Ti ratio be from 1 to 1000.

The electron-donor compounds that can be used as external donors include aromatic acid esters such as alkyl benzoates, and in particular silicon compounds containing at least one Si-OR bond, where R is a hydrocarbon radical.

Examples of silicon compounds are (tert-butyl)<sub>2</sub> Si (OCH<sub>3</sub>)<sub>2</sub>, (cyclohexyl) (methyl) Si (OCH<sub>3</sub>)<sub>2</sub>, (phenyl)<sub>2</sub> Si (OCH<sub>3</sub>)<sub>2</sub> and (cyclopentyl)<sub>2</sub> Si (OCH<sub>3</sub>)<sub>2</sub>. 1,3-diethers having the formulae described above can also be used advantageously. If the internal donor is one of these diethers, the external donors can be omitted.

The catalysts can be pre-contacted with small amounts of olefins (prepolymerization).

Other catalysts that may be used in the process according to the present invention are metallocene-type catalysts, as described in USP 5,324,800 and EP-A-0 129 368; particularly advantageous are bridged bis-indenyl metallocenes, for instance as described in USP 5,145,819 and EP-A-0 485 823. Another class of suitable catalysts are the so-called constrained geometry catalysts, as described in EP-A-0 416 815 (Dow), EP-A-0 420 436 (Exxon), EP-A-0 671 404, EP-A-0 643 066 and WO 91/04257. These metallocene

compounds may be used in particular to produce the copolymers (a) and (b).

The compositions of the present invention can also be obtained by preparing separately the said components 1) and 2) or even copolymers (a), (b) and component 1), by operating with the same catalysts and substantially under the same polymerization conditions as previously explained (except that a wholly sequential polymerization process will not be carried out, but the said components and fractions will be prepared in separate polymerization steps) and then mechanically blending said components and fractions in the molten or softened state. Conventional mixing apparatuses, like screw extruders, in particular twin screw extruders, can be used.

The compositions of the present invention can also contain additives commonly employed in the art, such as antioxidants, light stabilizers, heat stabilizers, nucleating agents, colorants and fillers.

In particular, the addition of nucleating agents brings about a considerable improvement in important physical-mechanical properties, such as Flexural Modulus, Heat Distortion Temperature (HDT), tensile strength at yield and transparency.

Typical examples of nucleating agents are the p-tert.-butyl benzoate and the 1,3- and 2,4-dibenzylidenesorbitols.

The nucleating agents are preferably added to the compositions of the present invention in quantities ranging from 0.05 to 2% by weight, more preferably from 0.1 to 1% by weight with respect to the total weight.

The addition of inorganic fillers, such as talc, calcium carbonate and mineral fibers, also brings about an improvement to some mechanical properties, such as Flexural Modulus and HDT. Talc can also have a nucleating effect.

The particulars are given in the following examples, which are given to illustrate, without limiting, the present invention.

#### **Examples 1-13**

In the following examples polyolefin compositions according to the present invention are prepared by sequential polymerization.

The solid catalyst component used in polymerization is a highly stereospecific Ziegler-Natta catalyst component supported on magnesium chloride, containing about 2.5% by weight of titanium and diisobutylphthalate as internal donor, prepared by analogy with the method described in Example 1 of European published patent application 395083.

### **CATALYST SYSTEM AND PREPOLYMERIZATION TREATMENT**

Before introducing it into the polymerization reactors, the solid catalyst component described above is contacted at 13 °C for 20 minutes with aluminum triethyl (TEAL) and dicyclopentylmethoxysilane (DCPMS), in a TEAL/DCPMS weight ratio equal to about 3 and in such quantity that the TEAL/solid catalyst component weight ratio be equal to around 14.

The catalyst system is then subjected to prepolymerization by maintaining it in suspension in liquid propylene at 20 °C for about 5 minutes before introducing it into the first polymerization reactor.

### **POLYMERIZATION**

The polymerization runs are conducted in continuous in a series of four reactors equipped with devices to transfer the product from one reactor to the one immediately next to it. The first and second reactors are liquid phase reactors, and the third and fourth are gas phase reactors.

Hydrogen is used as molecular weight regulator.

The gas phase (propylene, ethylene, butene and hydrogen) is continuously analyzed via gas-chromatography.

At the end of the run the powder is discharged, stabilized following known techniques, and dried in an oven at 60 °C under a nitrogen flow.

Then the polymer particles are introduced in a rotating drum, where they are mixed with 0.01% by weight of Irgafos 168 tris (2,4-di-tert-butylphenyl) phosphite, 0.05% by weight of Irganox 1010 pentaerythrityl-tetrakis [3-(3,5-di-tert-butyl-4-hydroxy-phenyl)] propionate and 0.18% by weight of Millad 3988 3,4-dimethylbenzylidene sorbitol.

Then the polymer particles are introduced in a twin screw extruder Berstorff ZE 25 (length/diameter ratio of screws: 33) and extruded under nitrogen atmosphere in the following conditions:

Rotation speed:	250 rpm;
Extruder output:	6-20 kg/hour;
Melt temperature:	200-250 °C.

The data relating to the final polymer compositions reported in the tables are obtained from measurements carried out on the so extruded polymers.

The data shown in the tables are obtained by using the following test methods.

- **Molar ratios of the feed gases**

Determined by gas-chromatography.

- **Ethylene and 1-butene content of the polymers**

Determined by I.R. spectroscopy.

- **Melt Flow Rate MFR**

Determined according to ASTM D 1238, condition L.

- **Xylene soluble and insoluble fractions**

Determined as follows.

2.5 g of polymer and 250 cm<sup>3</sup> of xylene are introduced in a glass flask equipped with a refrigerator and a magnetical stirrer. The temperature is raised in 30 minutes up to the boiling point of the solvent. The so obtained clear solution is then kept under reflux and stirring for further 30 minutes. The closed flask is then kept for 30 minutes in a bath of ice and water and in thermostatic water bath at 25 °C for 30 minutes as well. The so formed solid is filtered on quick filtering paper. 100 cm<sup>3</sup> of the filtered liquid is poured in a previously weighed aluminum container which is heated on a heating plate under nitrogen flow, to remove the solvent by evaporation. The container is then kept in an oven at 80 °C under vacuum until constant weight is obtained. The weight percentage of polymer soluble in xylene at room temperature is then calculated. The percent by weight of polymer insoluble in xylene at room temperature is considered the Isotacticity Index of the polymer. This value corresponds substantially to the Isotacticity Index determined by extraction with boiling n-heptane, which by definition constitutes the Isotacticity Index of polypropylene.

- **Intrinsic Viscosity (I.V.)**

Determined in tetrahydronaphthalene at 135 °C.

- **Melting temperature (Tm)**

Determined by DSC (Differential Scanning Calorimetry).

- **Flexural Modulus**

Determined according to ISO 178.

- **Tensile stress at yield**

Determined according to ISO R 527.

- **Elongation at yield**

Determined according to ISO R 527.

**Tensile stress at break**

Determined according to ISO R 527.

**Elongation at break**

Determined according to ISO R 527.

**Izod impact strength (notched)**

Determined according to ISO 180/1A

**Ductile/Brittle transition temperature (D/B)**

Determined according to internal method MA 17324, available upon request.

According to this method, the bi-axial impact resistance is determined through impact with an automatic, computerised striking hammer.

The circular test specimens are obtained by cutting with circular hand punch (38 mm diameter). They are conditioned for at least 12 hours at 23°C and 50 RH and then placed in a thermostatic bath at testing temperature for 1 hour.

The force-time curve is detected during impact of a striking hammer (5.3 kg, hemispheric punch with a ½" diameter) on a circular specimen resting on a ring support. The machine used is a CEAST 6758/000 type model no. 2.

D/B transition temperature means the temperature at which 50% of the samples undergoes fragile break when submitted to the said impact test.

**Preparation of the plaque specimens**

Plaques for D/B measurement, having dimensions of 127 x 127 x 1.5 mm are prepared according to internal method MA 17283; plaques for Haze measurement, 1 mm or 1.5 mm thick, are prepared by injection moulding according to internal method MA 17335 with injection time of 1 second, temperature of 230 °C, mould temperature of 40 °C, description of all the said methods being available upon request.

**Method MA 17283**

The injection press is a Negri Bossi type (NB 90) with a clamping force of 90 tons.

The mould is a rectangular plaque (127x127x1.5mm).

The main process parameters are reported below:

Back pressure (bar): 20

Injection time (s): 3

Maximum Injection pressure (MPa):	14
Hydraulic injection pressure (MPa):	6-3
First holding hydraulic pressure (MPa):	4±2
First holding time (s):	3
Second holding hydraulic pressure (MPa):	3±2
Second holding time (s):	7
Cooling time (s):	20
Mould temperature (°C):	60

The melt temperature is between 220 and 280 °C.

#### Method MA 17335

The injection press is a Battenfeld type BA 500CD with a clamping force of 50 tons.

The insert mould leads to the moulding of two plaques (55x60x1 or 1.5 mm each).

#### Haze on plaque

Determined according to internal method MA 17270, available upon request.

The plaques are conditioned for 12 to 48 hours at R.H. 50±5% and 23±1°C.

The apparatus used is a Hunter D25P-9 colorimeter. The measurement and computation principle are given in the norm ASTM-D1003.

The apparatus is calibrated without specimen, the calibration is checked with a haze standard. The haze measurement is carried out on five plaques.

TABLE 1

		Ex. 1	Ex. 2	Ex. 3
<b>1<sup>st</sup> L.P.R.</b>				
Temperature	°C	70	70	70
MFR "L"	g/10 <sup>3</sup>	26	23	29
C2 content (polymer)	wt%	1.4	1.3	1.3
Xylene insoluble	wt%	96.6	96.1	97.1
<b>2<sup>nd</sup> L.P.R.</b>				
Temperature	°C	70	70	70
MFR "L"	g/10 <sup>3</sup>	29	25	25.2
C2 content (total)	wt%	1.4	1.3	1.2
Xylene insoluble	wt%	96.6	96.1	97.1
<b>1<sup>st</sup> G.P.R.</b>				
Temperature	°C	85	85	85
Pressure	MPa	1.6	1.6	1.6
H <sub>2</sub> /C2-	mol	0.13	0.2	0.16
C2-/(C2-+C3-)	mol	0.16	0.162	0.16
MFR "L"	g/10 <sup>3</sup>	17.2	18.7	16.7
C2 content (polymer)	wt%	31	24.6	26.5
Xylene soluble	wt%	15.4	17.1	16.7
Split	wt%	12.5	13	14
<b>2<sup>nd</sup> G.P.R.</b>				
Temperature	°C	85	85	85
Pressure	MPa	1.9	1.9	1.9
H <sub>2</sub> /C2-	mol	0.15	0.26	0.31
C4-/(C4-+C2-)	mol	0.35	0.35	0.35
MFR "L"	g/10 <sup>3</sup>	11.6	10	13.2
C2 content (polymer)	wt%	85	85	85
Split	wt%	11.5	17	13

TABLE 1 (cont.)

		Ex. 1	Ex. 2	Ex. 3
<b>FINAL PRODUCT</b>				
Xylene soluble	wt%	15.4	17.6	17.1
X.S. I.V.	dl/g	1.96	1.69	1.65
MFR "L"	g/10'	12	13	14
C2 content (polymer)	wt%	15.4	18.7	16
C4 content (polymer)	wt%	<2	2.3	<2
Izod at 23 °C	KJ/m <sup>2</sup>	14.4	13.1	8.3
Flexural modulus	MPa	880	900	1030
D/B transition temperature	°C	-47	-37	-32
Haze, 1.5 mm plaque	%	89	65	65

TABLE 2

		Ex. 4	Ex. 5	Ex. 6
<b>1<sup>st</sup> L.P.R.</b>				
Temperature	°C	67	67	66
MFR "L"	g/10'	33	29	32
C2 content (polymer)	wt%	1.6	1.7	1.5
Xylene insoluble	wt%	96.5	96.2	95.7
<b>2<sup>nd</sup> L.P.R.</b>				
Temperature	°C	67	67	67
MFR "L"	g/10'	33	29	32.6
C2 content (total)	wt%	1.5	1.4	1.3
Xylene insoluble	wt%	96.5	96.2	96
<b>1<sup>st</sup> G.P.R.</b>				
Temperature	°C	75	80	75
Pressure	MPa	1.6	1.6	1.6
H <sub>2</sub> /C2-	mol	0.26	0.3	0.36
C2-/(C2-+C3-)	mol	0.16	0.165	0.16
MFR "L"	g/10'	18	19.1	22.7
C2 content (polymer)	wt%	27	29	28
Xylene soluble	wt%	18	16.8	17.4
Split	wt%	14	12	13
<b>2<sup>nd</sup> G.P.R.</b>				
Temperature	°C	80	80	80
Pressure	MPa	1.9	1.9	1.9
H <sub>2</sub> /C2-	mol	0.35	0.34	0.32
C4-/(C4-+C2-)	mol	0.35	0.373	0.37
MFR "L"	g/10'	13.6	15.2	15.2
C2 content (polymer)	wt%	85	85	85
Split	wt%	20	18.6	19

TABLE 2 (cont.)

		Ex. 4	Ex. 5	Ex. 6
<b>FINAL PRODUCT</b>				
Xylene soluble	wt%	17.7	18.9	19.3
X.S. I.V.	dl/g	1.55	1.5	1.48
MFR "L"	g/10 <sup>3</sup>	14	15	15
C2 content (polymer)	wt%	21.5	20.4	21.1
C4 content (polymer)	wt%	<2	2.5	2.5
Izod at 23 °C	KJ/m <sup>2</sup>	27.6	29.1	27.9
Flexural modulus	MPa	820	845	810
D/B transition temperature	°C	-38	-37	-38
Haze, 1.5 mm plaque	%	50	47	47

TABLE 3

		Ex. 7	Ex. 8	Ex. 9
<b>1<sup>st</sup> L.P.R.</b>				
Temperature	°C	66	66	66
MFR "L"	g/10'	26	30	29.3
C2 content (polymer)	wt%	1.4	1.5	1.7
Xylene insoluble	wt%	95.7	96.3	96.3
<b>2<sup>nd</sup> L.P.R.</b>				
Temperature	°C	67	67	67
MFR "L"	g/10'	25.8	31	31.3
C2 content (total)	wt%	1.4	1.5	1.6
Xylene insoluble	wt%	96	96	96
<b>1<sup>st</sup> G.P.R.</b>				
Temperature	°C	75	75	75
Pressure	MPa	1.6	1.6	1.6
H <sub>2</sub> /C2-	mol	0.375	0.364	0.38
C2-/(C2-+C3-)	mol	0.156	0.157	0.166
MFR "L"	g/10'	18.9	22.4	22
C2 content (polymer)	wt%	25.6	30	27.6
Xylene soluble	wt%	18.7	17.2	17.1
Split	wt%	14	13	13
<b>2<sup>nd</sup> G.P.R.</b>				
Temperature	°C	80	80	80
Pressure	MPa	1.9	1.9	1.9
H <sub>2</sub> /C2-	mol	0.37	0.409	0.439
C4-/(C4-+C2-)	mol	0.366	0.371	0.364
MFR "L"	g/10'	12.7	17.5	17.7
C2 content (polymer)	wt%	85	85	85
Split	wt%	21	19	17.5

TABLE 3 (cont.)

		Ex. 7	Ex. 8	Ex. 9
<b>FINAL PRODUCT</b>				
Xylene soluble	wt%	20.7	19.2	20.3
X.S. I.V.	dl/g	1.35	1.22	1.39
MFR "L"	g/10 <sup>3</sup>	14	17	19
C2 content (polymer)	wt%	22.6	20.9	19.4
C4 content (polymer)	wt%	2.8	2.7	2.3
Izod at 23 °C	KJ/m <sup>2</sup>	34.7	26.5	21.6
Flexural modulus	MPa	760	830	900
D/B transition temperature	°C	-38	-33	-29
Haze, 1.5 mm plaque	%	45	45	-
Haze, 1 mm plaque	%	-	27	25

TABLE 4

		Ex. 10	Ex. 11	Ex. 12	Ex. 13
<b>1<sup>st</sup> L.P.R.</b>					
Temperature	°C	65	65	65	65
MFR "L"	g/10'	28.9	32.5	31.4	65
C2 content (polymer)	wt%	1.6	1.4	1.6	-
Xylene insoluble	wt%	96.1	96.1	95.8	97.5
<b>2<sup>nd</sup> L.P.R.</b>					
Temperature	°C	65	65	65	65
MFR "L"	g/10'	30.5	30.6	30	70
C2 content (total)	wt%	1.2	1.2	1.4	-
Xylene insoluble	wt%	96.4	96.4	95.9	97.5
<b>1<sup>st</sup> G.P.R.</b>					
Temperature	°C	75	75	75	75
Pressure	MPa	1.6	1.6	1.6	1.6
H <sub>2</sub> /C2-	mol	0.36	0.399	0.393	0.4
C2-/(C2-+C3-)	mol	0.163	0.158	0.206	0.161
MFR "L"	g/10'	22.1	24	21	49
C2 content (polymer)	wt%	28	27	31	28
Xylene soluble	wt%	17.6	17.5	18.1	15.5
Split	wt%	13	13	14	12
<b>2<sup>nd</sup> G.P.R.</b>					
Temperature	°C	80	80	80	80
Pressure	MPa	1.9	1.9	1.9	1.9
H <sub>2</sub> /C2-	mol	0.423	0.422	0.44	0.424
C4-/(C4-+C2-)	mol	0.373	0.366	0.375	0.37
MFR "L"	g/10'	18.1	19.8	21	30.6
C2 content (polymer)	wt%	85	85	85	85
Split	wt%	19.5	18	18	18.5

TABLE 4 (cont.)

		Ex. 10	Ex. 11	Ex. 12	Ex. 13
<b>FINAL PRODUCT</b>					
Xylene soluble	wt%	20.3	19.9	22.3	18.4
X.S. I.V.	dl/g	1.18	1.19	1.22	1.27
MFR "L"	g/10'	18	18	19	29
C2 content (polymer)	wt%	21.2	19.8	22.8	19.2
C4 content (polymer)	wt%	3.2	3.2	2.9	3.2
Izod at 23 °C	KJ/m <sup>2</sup>	25	30	34	6.9
Flexural modulus	MPa	880	850	840	1040
Tensile stress at yield	MPa	21	20	19	23.5
Elongation at yield	%	17	18	18	14
Tensile stress at break	MPa	17.6	17	19.5	16
Elongation at break	%	380	355	440	120
D/B transition temperature	°C	-33	-35	-39	-35
Haze, 1mm plaque	%	22.5	26	28.7	29.3
Melting temperature	°C	155.9	156.6	157	164

Notes to the tables.

L.P.R. = Liquid Phase Reactor; Split = weight fraction of polymer produced in the specified reactor; G.P.R. = Gas Phase Reactor; C2 = ethylene; C4 = butene; H<sub>2</sub>/C2- = molar ratio of fed hydrogen to fed ethylene; C2-/(C2-+C3-) = molar ratio of fed ethylene to fed ethylene plus fed propylene; C4-/(C4-+C2-) = molar ratio of fed butene to fed butene plus fed ethylene; X.S. I.V. = Intrinsic Viscosity of Xylene Soluble fraction.

## CLAIMS

1. Polyolefin compositions comprising (percent by weight):
  - 1) 55%-90% of a crystalline propylene homopolymer or copolymer containing up to 15% of ethylene and/or C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s);
  - 2) 10%-45% of a blend of a copolymer of propylene with more than 15% up to 40% of ethylene (copolymer (a)), and a copolymer of ethylene with one or more C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s) containing from 10% to 40% of said C<sub>4</sub>-C<sub>10</sub>  $\alpha$ -olefin(s) (copolymer (b)), wherein the weight ratio (a)/(b) is from 1/4 to 4/1.
2. The polyolefin compositions of claim 1, having Melt Flow rate values (230 °C, 2.16 Kg) equal to or higher than 4 g/10 min.
3. The polyolefin compositions of claim 1, wherein the intrinsic viscosity of the fraction soluble in xylene at room temperature is in the range from 0.8 to 2.5 dl/g..
4. The polyolefin compositions of claim 1, wherein the content of polymer soluble in xylene at room temperature is less than 25%.
5. The polyolefin compositions of claim 1, having a Ductile/Brittle transition temperature equal to or lower than -25 °C.
6. A process for producing the polyolefin compositions of claim 1, carried out in at least three sequential steps, wherein in at least one polymerization step the relevant monomer(s) are polymerized to form component 1) and in the other two steps the relevant monomers are polymerized to form copolymers (a) and (b), operating in each step, except the first step, in the presence of the polymer formed and the catalyst used in the preceding step.
7. The process of claim 6, wherein the polymerization catalyst is a stereospecific Ziegler-Natta catalyst comprising, as catalyst-forming components, a solid component comprising a titanium compound having at least one titanium-halogen bond and an electron-donor compound, both supported on a magnesium halide in active form, and an organoaluminum compound.
8. The process of claim 6, wherein component 1) is prepared in liquid phase, and component 2) is prepared in gas phase.
9. Injection moulded articles comprising the polyolefin compositions of claim 1.

## INTERNATIONAL SEARCH REPORT

Internat	pplication No
PCT/EP 02/14068	

A. CLASSIFICATION OF SUBJECT MATTER		
IPC 7	C08L23/10	C08F297/08

According to International Patent Classification (IPC) or to both national classification and IPC
---

B. FIELDS SEARCHED
--------------------

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C08L C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
---

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT
--

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 353 981 A (MITSUI PETROCHEMICAL IND) 7 February 1990 (1990-02-07) examples 4-9 ---	1-5,9
Y		6-8
A	EP 0 792 814 A (LAMB AG) 3 September 1997 (1997-09-03) table 2 ---	1-5
Y	EP 0 844 279 A (MONTELL NORTH AMERICA INC) 27 May 1998 (1998-05-27) page 3, line 13-53 ---	6-8
X	EP 0 844 280 A (MITSUI CHEMICALS INC) 27 May 1998 (1998-05-27) example 2 ---	1-5,9
Y		6-8
		-/-

<input checked="" type="checkbox"/> Further documents are listed in the continuation of box C.
--

<input checked="" type="checkbox"/> Patent family members are listed in annex.
--

\* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*&\* document member of the same patent family

Date of the actual completion of the international search
---

14 February 2003
------------------

Date of mailing of the International search report
--

14/03/2003
------------

Name and mailing address of the ISA
-------------------------------------

European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl. Fax: (+31-70) 340-3016
---

Authorized officer
--------------------

Schmidt, H
------------

## INTERNATIONAL SEARCH REPORT

Intern:	Application No:
PCT/EP 02/14068	

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 316 966 A (IDEL KARSTEN ET AL) 23 February 1982 (1982-02-23) examples 1,2 -----	6-8

## INTERNATIONAL SEARCH REPORT

Intern	Application No
PCT/EP	02/14068

Patent document cited in search report	Publication date	Patent family member(s)		Publication date
EP 0353981	A 07-02-1990	JP 2043242 A		13-02-1990
		JP 2600829 B2		16-04-1997
		AT 117006 T		15-01-1995
		AU 628361 B2		17-09-1992
		AU 3902589 A		08-02-1990
		CA 1340143 A1		24-11-1998
		DE 68920503 D1		23-02-1995
		DE 68920503 T2		04-05-1995
		EP 0353981 A2		07-02-1990
		ES 2065993 T3		01-03-1995
		GR 3015316 T3		30-06-1995
		KR 135604 B1		23-04-1998
		US 5115030 A		19-05-1992
EP 0792814	A 03-09-1997	DE 19607541 C1		03-07-1997
		EP 0792814 A1		03-09-1997
EP 0844279	A 27-05-1998	AU 722346 B2		27-07-2000
		AU 4537897 A		28-05-1998
		BR 9705063 A		25-05-1999
		CA 2222118 A1		26-05-1998
		CN 1183430 A		03-06-1998
		EP 0844279 A1		27-05-1998
		JP 10226738 A		25-08-1998
		US 5948867 A		07-09-1999
EP 0844280	A 27-05-1998	CA 2222076 A1		26-05-1998
		CN 1183432 A		03-06-1998
		DE 69711156 D1		25-04-2002
		DE 69711156 T2		14-11-2002
		EP 0844280 A1		27-05-1998
		JP 10212382 A		11-08-1998
		SG 65032 A1		25-05-1999
		TW 448209 B		01-08-2001
US 4316966	A 23-02-1982	JP 1357860 C		13-01-1987
		JP 56057814 A		20-05-1981
		JP 59050246 B		07-12-1984
		AT 6518 T		15-03-1984
		CA 1142677 A1		08-03-1983
		DE 3066855 D1		12-04-1984
		EP 0027386 A1		22-04-1981